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Physico-chemical properties of the water-soluble C_{70}-tris-malonic solutions

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ABSTRACT

The paper presents some data on physico-chemical study of the C_{70}-carboxyfullerene water solutions. The data on temperature dependence of solubility in water, concentration dependence of density, specific conductivity, molar conductivity, dissociation constant, and dynamic light scattering are presented and characterized; composition of equilibrium solid phase in binary C_{70}-carboxyfullerene + water system is determined.

1. Introduction

Currently water soluble derivatives of light fullerenes (C_{60} and C_{70}) have a lot of potential ways of application in various fields of science and technology in particular in biology and medicine due to promising biological activity of such compounds (DNA photocleavage, HIV-Protease (HIV-P) inhibition, neuroprotection and apoptosis) [1–12].

The present paper is devoted to physico-chemical investigation of water solutions of the C_{70}-carboxyfullerene — $C_{70}[(C(COOH)_2]_3$ (i.e. isothermal and temperature dependencies of densities, concentration dependence of the refractive index, specific and equivalent conductivities, as well as the investigation of solubility of the C_{70} tris-malonic derivative in water). Analysis of literature reveals the lack of the experimental data devoted to investigation of physico-chemical properties of water-soluble derivatives of fullerenes and there solutions although such kind of research is a basis for the developing and optimization of the water-soluble fullerenes derivatives application. We can cite only several papers devoted to physico-chemical study of the water-soluble fullerenols, C_{60}-carboxyfullerene and amino acid derivatives of C_{60} water solutions [13–22].

The actuality of the carboxyfullerene investigation is mainly connected with the variety of application methods in biology and medicine. Let's dwell on briefly on the main results obtained in this field. Dugan et al. determined that carboxy-fullerene is a first-in-class functionalized water-soluble fullerene that reduces oxygen radical species associated with neurodegeneration in in vitro studies. This fact can be used in the creation of medicinal drug against Parkinson disease [23]. Authors of [24,25] have addressed their efforts on investigating the cytoprotective effect of carboxyfullerenes on H_2O_2-injured cells. The results show that C_{70}-carboxyfullerenes exhibit an obviously protective effect against oxidative stress on C2C12 cells at concentrations as low as $2.5 \cdot 10^{-6}$ mol dm^{-3}, whereas C_{60}-carboxyfullerenes show a protective effect at a relatively higher concentration ($4 \cdot 10^{-5}$ mol dm^{-3}). Further study reveals that C_{70}-carboxyfullerenes could enter into cells and mainly localize into the lysosome, which possibly involves the protective mechanism by stabilizing lysosome. The use of a significantly low concentration of C_{70}-carboxyfullerene as the antioxidative agent will benefit the therapeutic approaches aiming at alleviating ROS-induced injuries such as muscle disorder and arthritis. Liu et al. has

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tested carboxyfullerenes with different adduct numbers and cage sizes as photosensitizers for photodynamic therapy (PDT). It was determined that the photodynamic efficiency of carboxyfullerenes depends mainly on the cage size, and to a lesser extent on the adduct numbers. In particular, C_{70}-carboxyfullerenes are more efficient than C_{60}-carboxyfullerenes. Since C_{70}-carboxyfullerene displays an efficient PDT property and negligible cytotoxicity, it is promising for use in PDT applications, especially in vascular capillary diseases [26]. Li et al. showed that a bis-adduct malonic acid derivative of fullerene C_{60} inhibits tumor necrosis factor alpha-initiated cellular apoptosis via stabilizing lysosomes. It was determined that $C_{60}(C(COOH)_2)_2$ nanoparticles can protect cells by stabilizing lysosomal membranes via both upregulated expression of Hsp 70 and by their interactions with lysosomal membranes [27]. Rebecca et al. applied systematic and multipronged approach for material characterization and employing critical biological endpoints for determination of the impact of the physicochemical properties of carboxyfullerenes on cellular interactions. Authors revealed the ability of carboxyfullerenes to regulate intracellular oxidative stress, necrosis and apoptosis in human monocytic THP1 cells [28]. Authors of [29,30] carried out a structure–activity study on different carboxyfullerene superoxide dismutase (SOD) mimetics with distinct electronic and biophysical characteristics. These results indicate that the SOD activity of these cell-permeable compounds predicts neuroprotection, and establishes a structure–activity relationship. Authors of [31,32] have examined the effects of carboxyfullerenes on the cerebral ischemia-induced infarct volume, and on extracellular glutamate accumulation in an anesthetized rat brain cortex. It was determined that administering of carboxyfullerene significantly decreases the infarct volume and ischemia-induced extracellular glutamate accumulation. These results suggest that carboxyfullerene can protect a cerebral ischemia-induced infarct. This protective effect may be related to the attenuation of the accumulation of extracellular excitatory amino acids such as glutamate.

2. Experimental

2.1. Materials

Carboxyfullerene $C_{70}[(C(COOH)_2]_3$ of mass fraction purity 99.5% was used for the physico-chemical investigation of water solutions. The reagent was produced at ZAO "ILIP" (St. Petersburg). Additionally we have carried out the identification of the purchased $C_{70}[(C(COOH)_2]_3$ using the complex of the physico-chemical methods such as IR- and UV-spectroscopy, mass-spectrometry, and elemental analysis.

2.2. Apparatus and procedures

The measurements of the concentration dependence of density of the $C_{70}[(C(COOH)_2]_3$ aqueous solutions were performed by the pycnometer method. We used quartz pycnometer, volume calibration was performed with distilled water, the accuracy of temperature control during the density measurement was $\Delta T = \pm 0.1 \div 0.2$ K, and the accuracy of densities determination is equal to $\Delta\rho = \pm 0.001$ g·cm^{-3}. The series of the $C_{70}[(C(COOH)_2]_3$ water solutions were prepared by dilution of the basic solution at 298.15 ± 0.05 K.

The concentration dependence of refractive index of the $C_{70}[(C(COOH)_2]_3$ water solutions (n_D^{20}) was measured by refractometry using Abbe refractometer IRF-454B2M (measurement limits in transmission light $n_D^{25} = 1.3$–1.7, $\Delta n_D^{20} = \pm 0.0001$, the accuracy of temperature control $\Delta T = \pm 0.2$ K).

The temperature dependence of the $C_{70}[(C(COOH)_2]_3$ solubility in water in the temperature range 293.15–353.15 K was carried by the method of isothermal saturation in ampules. The saturation time was equal to 8 h, temperature was maintained with accuracy equal to ±0.05 K. For the $C_{70}[(C(COOH)_2]_3$ water solution saturation the thermostatic shaker (LAUDA ET 20) was used at a shaking frequency $\omega \approx 80$ c^{-1} and quantitative determination of the $C_{70}[(C(COOH)_2]_3$ concentrations in water was performed using a spectrophotometric technique at 330 nm (after the dilution and cooling of saturated solutions). The relative uncertainty of the solubility determination is equal to ±5%. Relative air humidity was 40–50%.

For the thermogravimetric investigation of the $C_{70}[(C(COOH)_2]_3$ derivative we have used NETZSCH STA 449F3STA449F3A-0483-M apparatus, the temperature range was 293.15–873.15 K at the air and the heating rate was 5 K·min^{-1}.

For determination of the specific conductivity of the $C_{70}[(C(COOH)_2]_3$ water solutions the Cyber Scan PC-300 measuring device was used. The relative uncertainty of the specific conductivity determination is equal ±1%. The solutions used were saturated by atmospheric air.

The $C_{70}[(C(COOH)_2]_3$ nanoparticle size distributions in aqueous solutions of different concentration measurements were carried out by the dynamic light scattering with the help of a Malvern Zetasizer 3000 (Great Britain) device.

3. Results and discussions

3.1. Isothermal solution densities

Experimental data on isothermal solution densities of the $C_{70}[C(COOH)_2]_3$ derivative are presented in Fig. 1. Concentration dependence of average molar volume ($\overline{V}$) of the solution components were calculated, according to classical thermodynamic Eq. (1):

$$\overline{V} = \frac{V}{n_{H_2O} + n_{C_{70}[C(COOH)_2]_3}}, \quad (1)$$

where: V is the volume of the $C_{70}[C(COOH)_2]_3$ water solution and n_{H_2O} and $n_{C_{70}[C(COOH)_2]_3}$ are the molar quantities of water and C_{70}-carboxyfullerene in 1 dm^3 of solution. The partial molar volumes of the solution components (V_{H_2O} and $V_{C_{70}[C(COOH)_2]_3}$) were calculated according to Eqs. (2) and (3) [33,34]:

$$V_{H_2O} = \left(\frac{\partial V}{\partial n_{H_2O}}\right)_{T,P,n_{C_{70}[C(COOH)_2]_3}} \qquad V_{C_{70}[C(COOH)_2]_3} = \left(\frac{\partial V}{\partial n_{C_{70}[C(COOH)_2]_3}}\right)_{T,P,n_{H_2O}}, \quad (2)$$

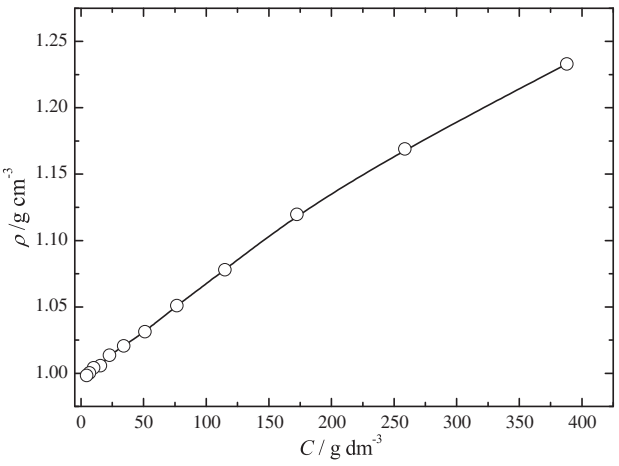

Fig. 1. Concentration dependence of the $C_{70}[C(COOH)_2]_3$ water solution density (ρ) at 298 K.

$$V_{H_2O} = \overline{V} - x_{C_{70}[C(COOH)_2]_3}\left(\frac{\partial \overline{V}}{\partial x_{C_{70}[C(COOH)_2]_3}}\right)_{T,P} V_{C_{70}[C(COOH)_2]_3} = \overline{V} - x_{H_2O}\left(\frac{\partial \overline{V}}{\partial x_{H_2O}}\right)_{T,P}. \quad (3)$$

Concentration dependence of average molar volume ($\overline{V}$) and partial molar volumes of the water solution components (V_{H_2O} and $V_{C_{70}[C(COOH)_2]_3}$) are represented in Figs. 2 and 3. One can see that in the area of diluted solutions the concentration dependence of the C_{70}-carboxyfullerene partial molar volume is rather complex. In the concentration range 0.002–0.003 the mole fraction dependence of the carboxyfullerene partial molar volume approaches to the molar volume of the solid $C_{70}[C(COOH)_2]_3$ and in the mole fraction range 10^{-5}–10^{-4} the $V_{C_{70}[C(COOH)_2]_3}$ ($x_{C_{70}[C(COOH)_2]_3}$) dependence extremely decreases and change the sign (becomes negative). The latest fact reveals that the addition of the first portions of the C_{70}-carboxyfullerene extremely compact and structure the solution.

3.2. Refraction of water solutions

Concentration dependence of the C_{70}-carboxyfullerene water solutions refraction index is presented in Fig. 4. Concentration dependencies of specific and molar refractions of the $C_{70}[C(COOH)_2]_3$ aqueous solutions at 298 K were calculated using Eqs. (4) and (5) [35,36].

$$r = \left(\frac{n_D^{25^2} - 1}{n_D^{25^2} + 2}\right)\frac{1}{\rho} \quad (4)$$

$$R = \left(\frac{n_D^{25^2} - 1}{n_D^{25^2} + 2}\right)\frac{\overline{M}}{\rho}, \quad (5)$$

where: r and R — are specific ($cm^3 \cdot g^{-1}$) and molar ($cm^3 \cdot mol^{-1}$) refractions and $\overline{M}$ — average molecular weight of solution: $\overline{M} = x_{H_2O} \cdot 18 + x_{C_{70}[C(COOH)_2]_3} \cdot 1146$ ($g \cdot mol^{-1}$). Concentration dependencies of molar and specific refractions are presented in Figs. 5 and 6. According to the rule of additivity of the solution refractions we can obtain Eqs. (6.1) and (6.2) [35,36]:

$$r = \left(r_{H_2O} \cdot w_{H_2O} + r_{C_{70}[C(COOH)_2]_3} \cdot w_{C_{70}[C(COOH)_2]_3}\right) \cdot \frac{1}{100}, \quad (6.1)$$

$$R = R_{H_2O} \cdot x_{H_2O} + R_{C_{70}[C(COOH)_2]_3} \cdot x_{C_{70}[C(COOH)_2]_3} \quad (6.2)$$

Fig. 3.1

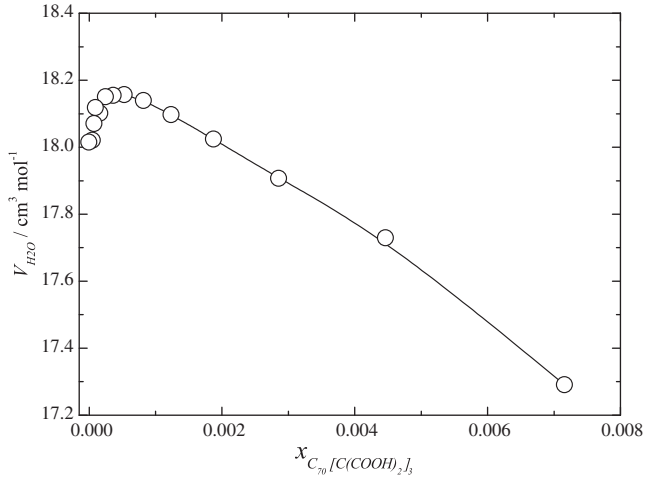

Fig. 3.2

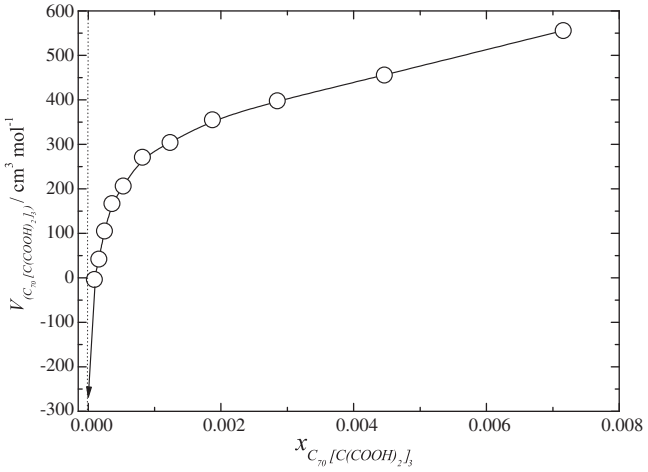

Fig. 3. Mole fraction dependence of the partial volumes (V_{H_2O} and $V_{C_{70}[C(COOH)_2]_3}$) of the solution components (3.1, 3.2) at 298.15 K.

where: r_i and R_i — specific and molar refraction of the i-th component and w_i and x_i — mass and molar fractions of the i-th component. Thus, using the value of water refraction we can easily calculate molar and specific refractions of the C_{70}-carboxyfullerene ($r_{C_{70}[C(COOH)_2]_3}$,

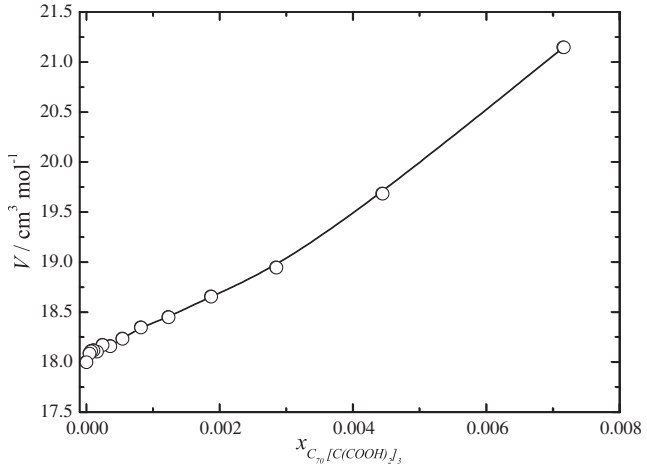

Fig. 2. Mole fraction ($x_{C_{70}[C(COOH)_2]_3}$) dependence of the average molar volume (V) of the C_{70}-carboxyfullerene water solution at 298 K.

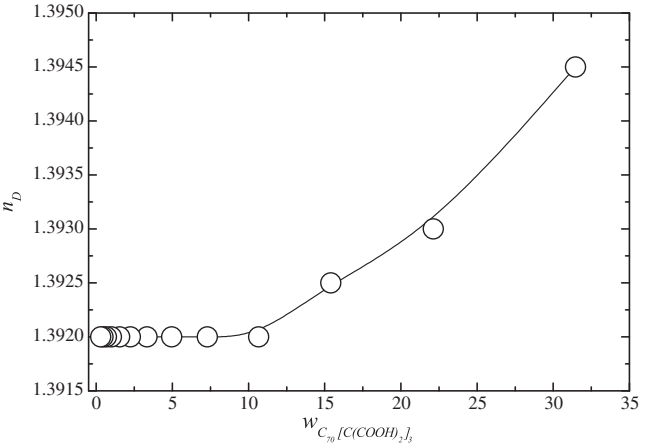

Fig. 4. Mass fraction ($w_{C_{70}[C(COOH)_2]_3}$) dependence of the C_{70}-carboxyfullerene water solution refraction index (n_D) at 298 K.

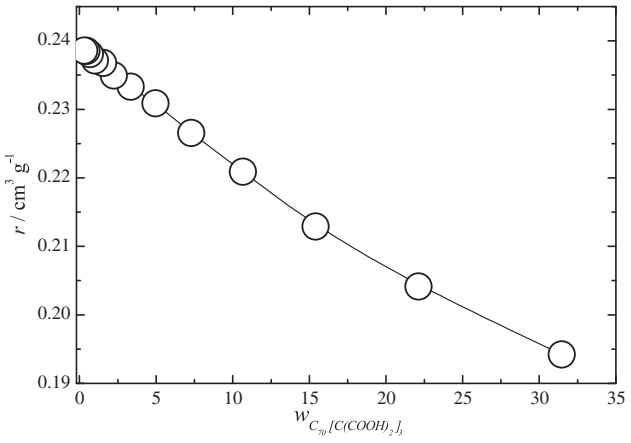

Fig. 5. Mass fraction ($w_{C_{70}[C(COOH)_2]_3}$) dependence of the C_{70}-carboxyfullerene water solution specific refraction (r) at 298 K.

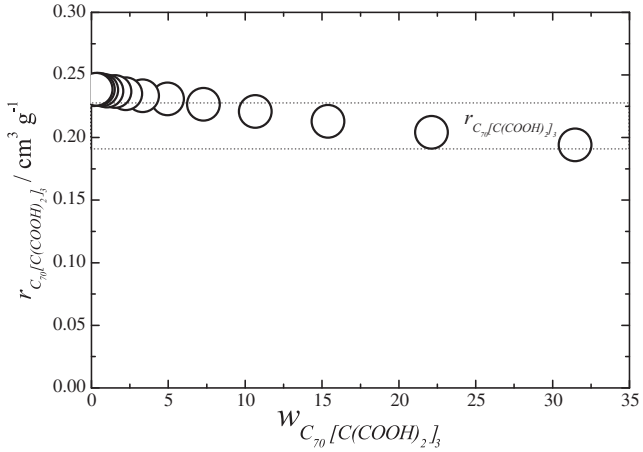

Fig. 7. Specific refraction of $C_{70}[C(COOH)_2]_3$ ($r_{C_{70}[C(COOH)_2]_3}$) in water solutions at 298 K.

$R_{C_{70}[C(COOH)_2]_3}$) (see Figs. 7 and 8). Figs. 7 and 8 show that both values of molar and specific refractions are constant, taking into account the fact that experimental data on refractions at low concentration of $C_{70}[C(COOH)_2]_3$ are characterized by comparatively low accuracy. We can also calculate the C_{70}-carboxyfullerene molar refraction according to another additivity rule [35] using the atomic refractions — $R_{i(j)}$ of i-th atom in j-th functional group:

$$R^{add} \approx 79R_c + 6R_{O(-OH)} + 6R_{O(=C=O)} + 6R_H \approx 219.5 \div 224.3\,cm^3 \cdot mol^{-1}. \quad (7)$$

The discrepancy in the molar refraction calculation is connected with the choice of the spectral lines: for the line $H_\alpha[\lambda = 658.3(nm)]$ — $R^{add} \approx 219.5\ cm^3 \cdot mol^{-1}$; and for the line $H_\gamma[\lambda = 436.1(nm)]$ — $R^{add} \approx 224.3\ cm^3 \cdot mol^{-1}$ [36]. Alternative calculation of the $C_{70}[C(COOH)_2]_3$ molar refraction can be performed using the refractions of functional groups — R_i (according to Fogel [36]):

$$R^{add} \approx 73R_c + 6R_{-COOH} \approx 229.4\,cm^3 \cdot mol^{-1}. \quad (8)$$

The C_{70}-carboxyfullerene molar refraction calculated from the obtained experimental data is equal to $R \approx 222–273\ cm^3 \cdot mol^{-1}$. The specific refraction of the C_{70}-carboxyfullerene can be calculated using Eq. (9):

$$r^{add} = \frac{R^{add}}{M(C_{70}[C(COOH)_2]_3)} \approx 0.191 \div 0.196 \div 0.200\,cm^3 \cdot g^{-1}. \quad (9)$$

The value of the $C_{70}[C(COOH)_2]_3$ specific refraction is very close to the specific refraction of water ($r^{add}(HOH) \approx 0.207\ cm^3 \cdot g^{-1}$). The C_{70}-carboxyfullerene specific refraction calculated from the obtained experimental data is equal to $r \approx 0.19–0.24\ cm^3 \cdot g^{-1}$.

3.3. Temperature dependence of the $C_{70}[C(COOH)_2]_3$ solubility in water and water solution densities

Temperature dependencies of the C_{70}-carboxyfullerene solubility and density in water are presented in Fig. 9. One can see the following: (i) the solubility values of $C_{70}[C(COOH)_2]_3$ are very high (thousands $g \cdot dm^{-3}$), such values correspond to the solubility of well-soluble phases as fullerenol-d or, for example halite — NaCl [37–39]; (ii) temperature dependence of solubility is non-monotonic, the solubility reaches maximum at 320 K (point O in Fig. 9); and (iii) the solubility diagram consists of 2 branches, corresponding to crystallization of different solid phases: ($C_{70}[C(COOH)_2]_3 \cdot 6H_2O$ and non-solvated $C_{70}[C(COOH)_2]_3$) and one nonvariant point (point O in

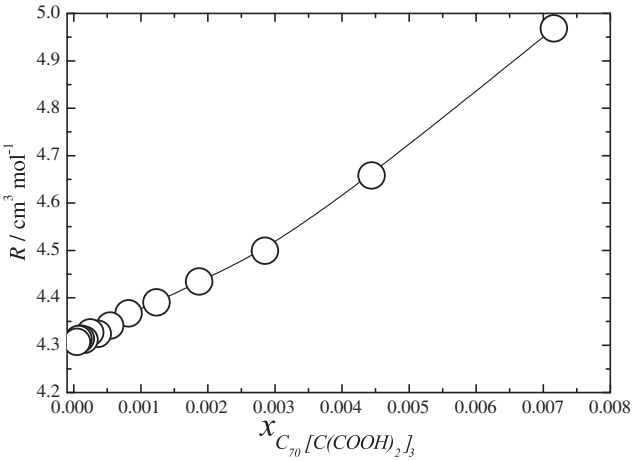

Fig. 6. Mole fraction dependence of the C_{70}-carboxyfullerene water solution molar refraction (R) at 298 K.

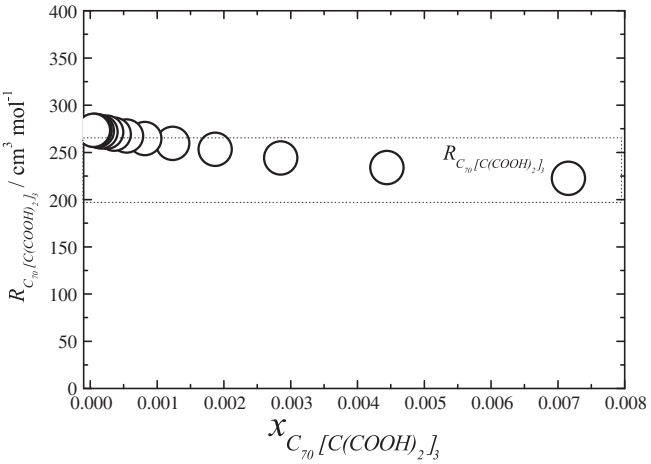

Fig. 8. Molar refraction ($R_{C_{70}[C(COOH)_2]_3}$) of $C_{70}[C(COOH)_2]_3$ in water solutions at 298 K.

Fig. 9.1

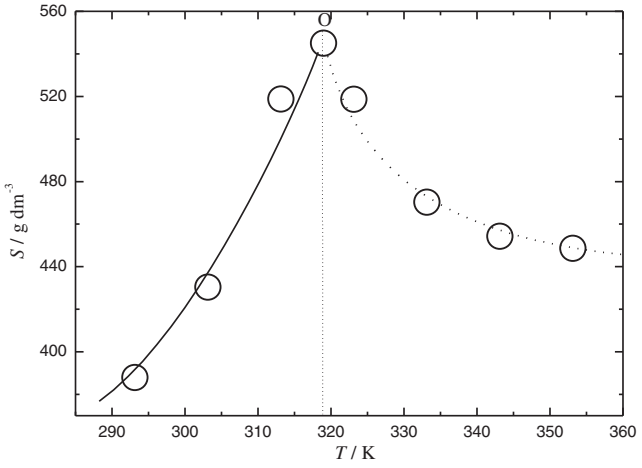

Fig. 9.2

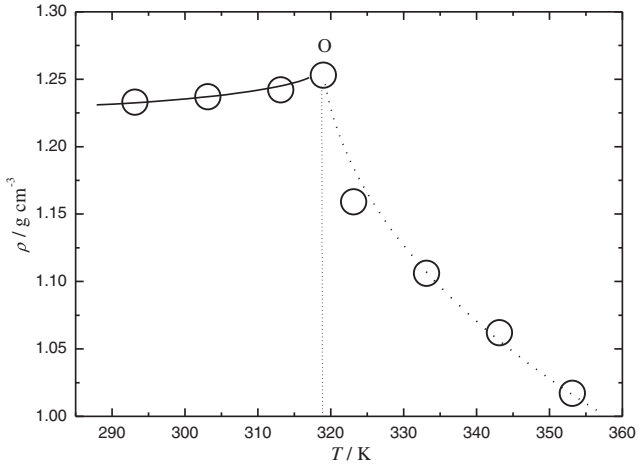

Fig. 9. Temperature dependence of solubility (S) (Fig. 9.1) and density (ρ) (Fig. 9.2) of the C_{70}-carboxyfullerene water solutions. Solid line corresponds to the crystallization of $C_{70}[C(COOH)_2]_3 \cdot 6H_2O$, dotted line corresponds to the crystallization of $C_{70}[C(COOH)_2]_3$. O is a nonvariant point corresponding to simultaneous saturation by both solid phases.

Fig. 9), corresponding to simultaneous saturation by both phases. Complex thermal analysis of the C_{70}-carboxyfullerene crystallohydrate in the temperature range 298–873 K is presented in Fig. 10 and the description of the thermal effects is presented in Table 1. Analogous multistage dehydration and decarboxylation we have observed earlier for the $C_{60}[(C(COOH)_2]_3$ crystallohydrate [21].

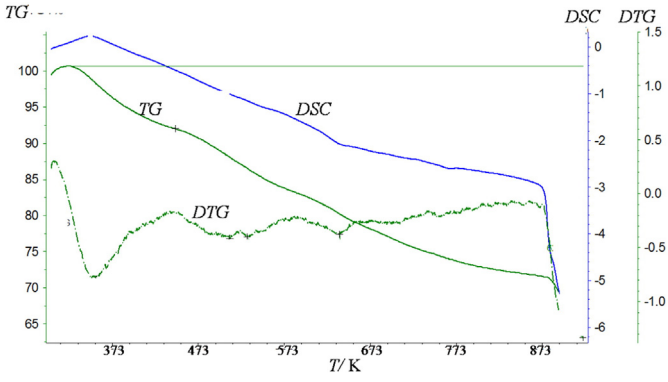

Fig. 10. Thermal analysis of the C_{70}-carboxyfullerene crystallohydrate.

3.4. Conductivity of water solutions of $C_{70}[C(COOH)_2]_3$

Concentration dependence of specific electric conductivity of the $C_{70}[(C(COOH)_2]_3$ water solutions at 298 K was investigated carrying out the measurement of the specific resistance of the solutions ρ ($\Omega \cdot$cm) [40]:

$$\kappa = \frac{1}{\rho}. \tag{10}$$

Specific electric conductivity corresponds to conductivity of the unit volume of solution located between two parallel planar electrodes (at the distance of 1 cm) with the surface equal to 1 cm. One can see (Table 2) that the dependence κ (C_M) (C_M is molarity of the $C_{60}[(C(COOH)_2]_3$ water solution) increases with increasing of concentration.

Molar electric conductivity ($\lambda - S \cdot cm^2 \cdot mol^{-1}$), i.e. conductivity of the electrolyte volume containing 1 mol of the solute was calculated using Eq. (11) [40]:

$$\lambda = \frac{1000\kappa}{C_M}, \tag{11}$$

where: C_M is the molarity of solution ($mol \cdot dm^{-3}$). Experimental data on molar conductivity are presented in Table 2. For the molar electric conductivity determination in the infinitely diluted solutions (λ_0) we have extrapolated the $\lambda(C_M{}^{1/2})$ dependence to $C_M{}^{1/2} = 0$, according to the Onsager equation [40]:

$$\lambda = \lambda_0 - A \cdot C_M^{1/2}, \tag{12}$$

where: A is a constant under conditions of experiment.

Apparent degree of dissociation α was calculated, according to Eq. (13) (neglecting by the ions transmission coefficients) [40]:

$$\alpha = \frac{\lambda}{\lambda_0}. \tag{13}$$

The calculated values of the apparent degree of dissociation are presented in Table 2 ($\lambda_0 \approx 1870\ S \cdot cm^2 \cdot mol^{-1}$).

The concentration dependence of concentration dissociation constant – K_D (see Table 2) was calculated according to the "Ostwald dilution law" (neglecting by activity coefficients of the ions and non-dissociated molecular – $\gamma_i = \gamma_\pm = 1$) [40]:

$$K_d = \frac{C_M \alpha^2}{(1-\alpha)}. \tag{14}$$

Thermodynamic dissociation constant – K_D^{therm} was calculated by extrapolation of $K_D(C_M)$ dependence to the region of infinitely diluted solution:

$$K_D^{therm} = \lim_{C_M \to 0}(K_D), \quad pK_D = -1\ gK_D. \tag{15}$$

According to our calculation $pK_D^{therm} = 3.67$.

3.5. Size distribution of the $C_{70}[C(COOH)_2]_3$ associates in water solutions

Experimental data on size distribution of the $C_{70}[C(COOH)_2]_3$ associates in water solutions are presented in Table 3. Estimation of the monomer $C_{70}[(C(COOH)_2]_3$ linear dimension (d_0) was performed from the refraction data. Molar refraction of the C_{70}-carboxyfullerene ($R(C_{70}[(C(COOH)_2]_3)$ is equal to 224 $cm^3 \cdot mol^{-1}$. Thus, we can easily calculate the volume of one molecule: $V_0(C_{70}[(C(COOH)_2]_3) \approx \frac{2.24 \cdot 10^{-4}}{6.02 \cdot 10^{23}} \approx 3.7 \cdot 10^{-27} m^3$/molecule. Using the spherical

Table 1
Complex thermal analysis of the $C_{70}[C(COOH)_2]_3$ crystallohydrate. T_b and T_f — temperatures of the beginning and finishing of the thermal effect, $\Delta m_i/m_0$ — the mass loss, m_0 — the initial mass.

No	$(T_b–T_f)$/K	Process	$\Delta m_i/m_0^{(calc)}$/%	$\Delta m_i/m_0^{(exp)}$/%
1	313–393	$C_{70}(C(COOH)_2)_3 \cdot 6H_2O \rightarrow C_{70}(C(COOH)_2)_3 + 6H_2O$	0.09	0.09
2–7	510–530	$C_{70}(C(COOH)_2)_3 \rightarrow C_{70}(CO)_3 + 6CO + 3H_2O$	0.19	0.20
	637–693			
	753–873			
8	880–918	$C_{70}(CO)_3 \rightarrow C_{70} + 3CO$	0.07	0.08

Table 2
Experimental data on electric conductivity of the $C_{70}[C(COOH)_2]_3$ water solutions.

C/g·dm^{-3}	M/mol·dm^{-3}	α	κ/S·cm^{-1}	λ/S·cm^2·mol^{-1}	pK_D
0.000	0.000	1.00 (extrapolation)	0.000	1870 (extrapolation)	3.67 (extrapolation)
0.125	$1.090 \cdot 10^{-4}$	0.71	$1.44 \cdot 10^{-4}$	1320	3.73
0.250	$2.18 \cdot 10^{-4}$	0.58	$2.34 \cdot 10^{-4}$	1080	3.77
0.500	$4.36 \cdot 10^{-4}$	0.53	$4.31 \cdot 10^{-4}$	989	3.59
1.000	$8.72 \cdot 10^{-4}$	0.48	$7.82 \cdot 10^{-4}$	897	3.41

approximation, the linear dimension (diameter of the carboxyfullerene molecule) can be calculated by the following way: $d_0(C_{70}[(C(COOH)_2]_3) \approx [\frac{6V_0}{\pi}]^{\frac{1}{3}} \approx 1.9 \cdot 10^{-9} m \approx 1.9 nm$.

The number of i-th type associates packed into $(i+1)$-th type associates — $N_{i \rightarrow i+1}$ was estimated by the following equation [41]:

$$N_{i \rightarrow i+1} = \left(\frac{d_{i+1}}{d_i}\right)^3 \cdot K_{pack}, \quad (16)$$

where: $K_{pack} \approx 0.52$ — is a formal packing coefficients for the case of "little spheres, packed in the large sphere" ($1 - K_{pack} \approx 0.48$ — is a volume fraction fulfilled by water molecules or empty volume). From the experimental and calculated data presented in Table 3 we can conclude the following: (i) we have not detected monomer molecules (with linear dimension ($\overline{d}_0$) equal to 1.9 nm) in all investigated solutions even in very diluted ($C = 0.01$ g·dm^{-3}); (ii) diameter of the first type associates (first order clusters of percolation) has the similar linear dimension ($\overline{d}_1$) equal to 10 ± 5 nm. First order clusters of percolation were detected only in comparatively concentrated solutions ($C = 5$–10 g·dm^{-3}); (iii) diameter of the second type associates (second order clusters of percolation) is equal to $\overline{d}_2 \approx 70 \pm 30$ nm. Second order clusters of percolation were detected in all studied solutions, corresponding to the concentration range 0.01–10 g·dm^{-3}; (iv) diameter of the third type associates (third order clusters of percolation) is equal to $\overline{d}_3 \approx 250 \pm 100$ nm, these associates were also detected in all studied solutions; (v) the fourth type associates (fourth order clusters of percolation) were detected in all studied solutions, the diameter of the associates is equal to $\overline{d}_4 \approx 5000 \pm 1000$ nm (5 ± 1 μm), moreover the intensity of the signal increases with increasing of the C_{70}-carboxyfullerene concentration in water solution. The formation of the associates with such gigantic dimensions proves the micro-heterogeneous nature of the C_{70}-carboxyfullerene water solutions; (vi) for the description of such facts in the association process the model of consequent hierarchical association model was used. We consider that monomer spherical molecular form first type spherical associates, than first type spherical associates form second type spherical associates, than second type spherical associates form third type spherical associates, than third type spherical associates form forth type spherical associates (the last one corresponds to the colloid heterogeneous system).

4. Conclusions

Novel physico-chemical properties of the C_{70}-carboxyfullerene water solutions were investigated. The concentration dependence of density was investigated by the pycnometer method; the average molar and partial volumes of the solution components were calculated at 298.15 K. By the isothermal saturation method the C_{70}-carboxyfullerene solubility in the distilled water in the temperature range 293.15 to 353.15 K was studied and the composition of the solid crystallohydrate was determined. The specific and molar conductivities, dissociation constant and apparent degree of dissociation were obtained for the C_{70}-carboxyfullerene water solutions. By the dynamic light scattering method, the average size of the C_{70}-carboxyfullerene associates was determined. The actuality of such investigation is closely connected with possibilities of application of the obtained results for the development and optimization of the water-soluble carboxyfullerene application in biology, medicine and material science.

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Table 3
Size distribution of the $C_{70}[(C(COOH)_2]_3$ associates in water solutions at 298 K. d_0, d_1, d_2, d_3, and d_4 — size distribution interval of the first, second, third and fourth type associate diameters. $N_{0 \rightarrow 1}$ — average number of monomer molecules of $C_{70}[(C(COOH)_2]_3$ in the first order clusters, $N_{1 \rightarrow 2}$ — average number of the first order clusters in the second order clusters, $N_{2 \rightarrow 3}$ — average number of the second order clusters in the third order clusters, $N_{3 \rightarrow 4}$ — average number of the third order clusters in the fourth order clusters.

C/g·dm^{-3}	d_0/nm	d_1/nm	d_2/nm	d_3/nm	d_4/μm	$N_{0 \rightarrow 1}$	$N_{1 \rightarrow 2}$	$N_{2 \rightarrow 3}$	$N_{3 \rightarrow 4}$
0.01	–	–	70 ± 30	250 ± 100	5 ± 1	–	200	20	4000
0.1	–	–	70 ± 30	250 ± 100	5 ± 1	–	250	25	4500
1.0	–	–	70 ± 30	250 ± 100	5 ± 1	–	250	25	5000
5.0	–	10 ± 5	70 ± 30	250 ± 100	5 ± 1	70	300	25	5000
10.0	–	10 ± 5	70 ± 30	250 ± 100	5 ± 1	90	300	30	5500

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